

# Solvent-induced symmetry breaking and second order phase transitions

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## Abstract

The triiodide ion is an example of a system where symmetry-breaking may be induced by a solvent. The Landau free energy is expected to have a similar form to that for the mean field Ising model, but with solvent strength rather than temperature as the control parameter determining whether there is symmetry breaking. In order to examine the possibility of critical phenomena we have studied the properties of the ion in solvents based on a model for water with charges scaled by a factor  $\lambda$ . As  $\lambda$  is increased the system changes from one with no symmetry breaking to one with strong symmetry breaking. The behavior of various quantities, including the Shannon entropy, as a function of  $\lambda$  show only weak maxima near the critical value of  $\lambda = \lambda_c$ . We examine the behavior of a simple model and show that divergences would only be expected in the limit of low temperatures, and the essential difference between the solvent-induced symmetry breaking and the mean field Ising model is that in the latter the observed quantity is an average over many spins, while in the former observations are made on individual molecules.

## 1 Introduction

In an earlier paper we showed that symmetry breaking could be induced in the triiodide ion by varying the solvent [1]. Experiments and simulations [3, 4, 5, 6, 7] suggest that protic solvents which can form hydrogen bonds with a negative ion cause symmetry breaking of the ion, so that the charge becomes concentrated at one end of the ion and the corresponding bond elongates. We suggested that one could draw an analogy between the mean field Ising model with free energy

$$F = a(T - T_0)\eta^2 + C\eta^4 \quad (1)$$

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and solvent induced symmetry breaking with

$$F = a(R_0 - R)\eta^2 + C\eta^4. \quad (2)$$

In these expressions  $F$  is the Landau free energy per molecule (or per spin),  $\eta$  is an order parameter and  $a$  and  $C$  are coefficients [2]. The Ising model has a critical point when the temperature  $T$  reaches  $T_0$ ; below this temperature the symmetry is broken to give domains with non-zero order parameters, while above this temperature the order parameter is equal to zero. Various critical phenomena, such as vanishing of the susceptibility and diverging fluctuations in the order parameter, are observed as the critical point is approached. As these mean-field critical phenomena result from the form of the equation for the free energy, it is interesting to see whether there are corresponding phenomena in the solvent-induced symmetry breaking. In this paper we describe an investigation of this point. In order to vary the solvent strength in a systematic way we used a series of modified waters as solvents. The models are based on the standard spc/e model with a Lennard-Jones center on the oxygen atom and charges on the atomic sites. The charges are scaled by a factor  $\lambda$  which varies from unity, giving the standard spc/e model which we know causes strong symmetry-breaking, to zero, giving a pure Lennard-Jones solvent which our earlier work shows does not cause symmetry breaking. Thus varying  $\lambda$  provides a method of tuning the solvent strength  $R$  through the critical value  $R_0$ .

## 2 Theory and computational details

### 2.1 Valence bond model for $\text{I}_3^-$

The model for triiodide ion is the same as used in our previous work [1, 6, 7, 8, 9]. The electronic structure of the ion is described using a semi-empirical valence bond model based on diatomics in molecules method [10] with additional terms due to the fact that the species is charged [11]. Provided the ion is constrained to be linear, its ground state is described by a  $3 \times 3$  Hamiltonian matrix, whose matrix elements depend on the instantaneous values of the bond lengths and the instantaneous external electrostatic potential due to the solvent. Full details are given in the appendix to reference [9]. The solvent molecules are rigid three-site models based on spc/e water [12], with partial charges on all three atomic sites and Lennard-Jones interactions on the oxygen site. The total energy of the system can be written as

$$E(\{r_i\}) = \sum_{\alpha\beta} c_{0\alpha}c_{0\beta}H_{\alpha\beta} + \sum_{ij} \frac{q_jq_k}{4\pi\epsilon_0r_{jk}} + \sum_{jk} V_{jk}^{LJ}(r_{jk}) + \sum_{jm} V_{jm}^{LJ}(r_{jm}). \quad (3)$$

where the first term is the quantum mechanical energy of the ground state, with  $H_{\alpha\beta}$  being the Hamiltonian matrix element between basis states  $\alpha$  and  $\beta$  and  $c_{0\alpha}$  the coefficient of basis state  $\alpha$  in the ground state. The second and third terms are sums of the electrostatic and Lennard-Jones interactions over all pairs of solvent sites  $j$  and  $k$ , and the last term is the sum of Lennard-Jones interactions between solvent sites and iodine atomic sites  $m$ .

Quantum mechanical forces on both iodine and solvent sites were calculated using the Hellman-Feynman theorem, while the forces arising from the three classical terms in equation (3) were calculated in the usual way within the molecular dynamics program. The ion was constrained to be linear throughout.

## 2.2 Modified water models

The solvent molecules were based on the standard spc/e model for a water molecule [12] with a Lennard-Jones center on the oxygen and charges on the atomic sites. In spc/e water hydrogen bonds and all other orientational correlations are due solely to electrostatic interactions between molecules. Thus the hydrogen-bond strength can be controlled by scaling the charges. In this study, nine solvent models were used with the charges were scaled by a factor  $\lambda$  which varied from 1.125, giving a super strong water, through 1, giving the standard spc/e model, to zero, giving a pure Lennard-Jones solvent.

The Lennard-Jones potential between the iodine and oxygen sites was the same as used in our previous work with water [1, 4, 6]. The Lennard-Jones parameters and the partial charges for sites are given in Table 1.

## 2.3 Simulation details

Molecular dynamics simulations were carried out using a version of the dlpol program [13] which was modified to include the construction and diagonalisation of the Hamiltonian matrix and the calculation of the Hellman-Feynman forces. The simulation cell contained one triiodide ion and 509 modified water molecules in a cubic box with an edge-length of 24.8Å. The density was the same for all simulations. Simulations were carried out at 300K with a time step of 1 fs. For each value of the charge scaling constant,  $\lambda$ , the system was thoroughly equilibrated before collecting data for 1 ns. Our earlier work showed that two order parameters were necessary to describe the symmetry breaking. The order parameters chosen are the molecular dipole moment  $\mu$  (relative to the center of mass) and the normal coordinate for the antisymmetric stretch  $\zeta = (b_{12} - b_{23})/\sqrt{6}$ . The former measures the extent of electronic distortion, while the latter measures the geometrical distortion. The instantaneous values of these parameters were determined at each time step, and averages, mean square fluctuations and probability histograms were constructed.

## 2.4 Shannon's information entropy

From the two-dimensional histograms for the probability distributions of the two order parameters, the Shannon information entropy function  $H(\zeta, \mu)$  was constructed for each bin

$$H(\zeta, \mu) = -p(\zeta, \mu) \ln p(\zeta, \mu), \quad (4)$$

where  $p(\zeta, \mu)$  is the probability of being in that bin, with  $\sum \sum p(\zeta, \mu) = 1$ . The Shannon entropy of the system [14] is then

$$h_S = \sum_{\zeta} \sum_{\mu} H(\zeta, \mu). \quad (5)$$

We show in the appendix that the limit of this sum as the bin sizes tend to zero is a property of the system, rather than of our information about it, and is the entropy associated with the spread of order parameter values. In our calculations the bin sizes used were  $\delta\mu = 3D$  and  $\delta\zeta = 0.04\text{\AA}$ . The values of the bin sizes affect the zero of entropy, but, as they were kept constant for all the simulations, entropy differences between runs are real although absolute values are arbitrary.

### 3 Results

Figure 1 shows the distribution of the Shannon entropy function  $H(\zeta, \mu)$  for selected values of  $\lambda$ . When  $\lambda$  is small there is a single maximum while when  $\lambda$  is large enough two maxima are seen. Figure 2 shows cross sections through this  $H$  surface for all the runs. The direction of cross section is different for each  $\lambda$  and is either chosen to go through the two maxima, or, when there is only a single maximum, it is chosen to go through the direction of minimum curvature. These figures show that there is symmetry breaking in the curve marked 4 ( $\lambda = 0.5$ ) and there is no symmetry breaking in the curve marked 3 ( $\lambda = 0.375$ ). Thus the critical value of  $\lambda$ ,  $\lambda_c$ , lies between these values, that is somewhat below  $\lambda = 0.5$ . These results confirm that varying the scaling parameter  $\lambda$  induces symmetry-breaking.

There is no a-priori reason to identify  $\lambda$  as opposed to some function of  $\lambda$  with the solvent strength in the free energy equation (2). However figure 3 shows the solvent-triiodide interaction energy (lowest curve). The interaction energy decreases smoothly with the scaling factor  $\lambda$  and is approximately linear in the critical region. This figure also shows (upper curve) the energetic cost of polarising the ion.

The inverse susceptibilities for the response to an external electric field

$$\chi^{-1} = kT / \langle \mu^2 \rangle \quad (6)$$

is plotted in figure 4. It can be seen that there is a monotonic decrease in the inverse susceptibility as a function of the scaling factor  $\lambda$ , and that  $\chi^{-1}$  does not tend to zero near the critical value  $\lambda = \lambda_c$ . In a second-order phase transition, however, inverse susceptibilities do tend to zero at the critical point.

The Shannon entropy,  $h_S$ , would also be expected to show critical behavior at the critical point. Figure 5 shows that in our system this quantity has a weak maximum at a value of  $\lambda$  which is slightly greater than the critical value  $\lambda_c$ , rather than diverging at  $\lambda_c$ .

### 4 Discussion

As the two figures 5, and 4 do not show the expected critical behavior near the critical value of the scaling constant,  $\lambda = \lambda_c$ , we conclude that there is a difference between our system and the mean field Ising model. In order to elucidate this difference we study the properties of a simple model.

#### 4.1 A simple model

Let us consider a simple model for symmetry breaking with a single order parameter  $\eta$  and a Landau free energy per molecule given by

$$\tilde{F} = a(R_0 - R)\tilde{\eta}^2 + C\tilde{\eta}^4. \quad (7)$$

This can be rewritten (by rescaling  $F = C\tilde{F}/(aR_0)^2$  and  $\eta^2 = C\tilde{\eta}^2/(2aR_0)$ ) as

$$F = (1 - \rho)\eta^2/2 + \eta^4/4, \quad (8)$$

where  $\rho = R/R_0$  is a measure of the relative strength of the solvent interaction. The critical point where symmetry breaking occurs is  $\rho = 1$ . In order to answer

the question as to when one should observe critical phenomena such as diverging fluctuations, we examine the properties of the probability distribution of the order parameter

$$p(\eta) = \exp[-\beta F]/Z = \exp[-\beta((1-\rho)\eta^2/2 + \eta^4/4)]/Z \quad (9)$$

as a function of the parameter  $\beta$ . In this expression

$$Z = \int_{-\infty}^{\infty} \exp[-\beta((1-\rho)\eta^2/2 + \eta^4/4)] d\eta. \quad (10)$$

Figure 6 shows the values of the entropy  $h = -\int p \ln p d\eta$  as a function of  $\rho$  for a number of values of  $\beta$ . It can be seen that the Shannon entropy has a maximum as a function of  $\rho$ . As  $\beta$  increases, this maximum gets sharper and shifts downwards towards  $\rho = 1$ .

For a second order phase transition, the inverse of the susceptibility  $\chi$ , which is given by  $\chi^{-1} = 1/\beta\langle\eta^2\rangle$ , tends to zero at the critical point where the phase transition occurs. The upper part of figure 7 shows the values of the inverse of the susceptibility of the model system as a function of  $\rho$  for a range of values of the parameter  $\beta$ . Again we observe that if  $\beta$  is large enough the inverse susceptibility decreases linearly towards a value of zero at  $\rho < 1$ . A simple calculation of the susceptibility above the critical value of  $\rho$  is misleading as the probabilities of positive and negative values of the order parameter are equal and the mean value is always 0. However if a small biasing field  $b$  is added giving the free energy

$$F = -b\eta + (1-\rho)\eta^2/2 + \eta^4/4, \quad (11)$$

then the lower part of figure 7 shows that the inverse susceptibility increases with  $\rho$  above the critical value  $\rho = 1$ .

The results at large  $\beta$  are very similar to those obtained from a mean field model of a second order phase transition with Landau free energy

$$F = -b\eta + a(T_0 - T)\eta^2/2 + C\eta^4/4. \quad (12)$$

In the standard treatment of this model [2], one is only concerned with the minima of the function. One finds that above the critical temperature  $T_0$  the minimum of  $F$  is at  $\eta_{min} = 0$  in the absence of an external field, while below  $T_0$  the minima are at  $\eta_{min} = \pm(a(T_0 - T)/C)^{1/2}$ . The susceptibility is calculated from the change of the position of  $\eta_{min}$  with the strength of the external field,  $\chi = d\eta_{min}/db$ . This gives

$$\begin{aligned} \chi^{-1} &= a(T - T_0) & T > T_0 \\ \chi^{-1} &= 2a(T_0 - T) & T < T_0. \end{aligned} \quad (13)$$

It will be noted that the standard treatment does not include fluctuations in the order parameter, while the expression that we have used (equation 9) gives the full range of possible values. The reason that one can ignore fluctuations in the treatment of phase transitions is that the expression for the free energy given in equation (12) is the free energy per unit cell or per spin. The observed  $\eta$  is the average over all the unit cells or all the spins and, as one observes the

average over a large number  $N$  of unit cells or over  $N$  spins, the probability of observing a given value of  $\eta$  is given by

$$p(\eta) = \exp[-(N/kT)(a(T_0 - T)\eta^2/2 + C\eta^4/4)]/Z. \quad (14)$$

In the limit  $N \rightarrow \infty$  it is indeed only the minima that are observed. In the solvation-induced symmetry breaking situation we observe individual molecules and the relevant probability is given by the similar equation 9 but with the difference that  $\beta = (4aR_0)^2/(CkT)$  rather than  $N/kT$ . The fact that we only see significant maxima in the Shannon entropy near the critical value of  $\rho$  when  $\beta$  is large is consistent with the fact that true critical phenomena only occur in the limit of  $N \rightarrow \infty$  and depend on the observation of an order parameter which is an average over many replicated systems. While solvent-induced symmetry breaking will never show true divergences, there will be maxima in the Shannon entropy if the value of the parameter  $(aR_0)^2/C$  is large enough compared to  $kT$ . Comparing the model results with those observed for the triiodide ion, we estimate that the order of magnitude of  $(aR_0)^2/CkT$  is about 100. At this value there is a weak maximum in the entropy at a higher solvent strength than the critical one and the inverse susceptibility decreases smoothly through the critical point.

## 5 Conclusion

In this paper we have examined the solvent-induced symmetry breaking induced by water and modified water. The use of scaled charges in the solvent models allows us to vary the solvent strength which induces the symmetry breaking continuously and to determine whether there are any phenomena analogous to critical phenomena. In this particular system the transition from no symmetry breaking to symmetry breaking is weak and there is only a small maximum in the Shannon entropy. By comparing the results to a simple model we see that if  $\beta = (aR_0)^2/CkT \approx 100$  the model system shows a rather similar behavior. In order to see significant critical behavior this parameter would need to be larger by a factor of 10 or more.

Although this example of solvent-induced symmetry breaking does not show critical effects, there may be other situations which do. A system which was less polarisable, would have a larger value of  $aR_0$ , but would need a strong interaction with the solvent for symmetry-breaking to occur at all.

## Acknowledgments

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## Appendix

Standard methods of statistical mechanics shows that in contact with a heat bath the probability  $p(\mathbf{r})d\mathbf{r}$  of observing the  $3N$  system coordinates  $\mathbf{r} = \{r_i\}$  with values between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$  is given by

$$p(\mathbf{r}) = \exp[-\beta H(\mathbf{r})]/Z, \quad (15)$$

where  $H$  is the potential energy.  $Z$  is the configurational integral for the complete system

$$Z = \int \exp[-\beta H(\mathbf{r})] d\mathbf{r} = \exp[-\beta F_{\text{conf}}], \quad (16)$$

which defines  $F_{\text{conf}}$ , the classical configurational part of the Helmholtz free energy of the system.

The total Helmholtz free energy can be written

$$F = -kT \ln Z - kT \ln A = F_{\text{conf}} + F_{\text{mom}} \quad (17)$$

where  $F_{\text{mom}} = -kT \ln A$  is an additional ideal term due to the momentum and indistinguishability,

$$A = \prod_i (2\pi m_i kT / h_i^2)^{3/2} / N_i! \quad (18)$$

where the product is over different types of atom,  $i$ .

Let us define the Landau free energy  $F_L(\eta)$  as the free energy of the system when an order parameters  $\eta(\mathbf{r})$  is constrained to a fixed value  $\eta_0$ . Thus

$$F_L(\eta_0) = -kT \ln \left[ \int \exp[-\beta H] \delta(\eta - \eta_0) d\mathbf{r} \right]. \quad (19)$$

From equation (15) we see that the probability  $p(\eta)d\eta$  of observing the value of the order parameter between  $\eta$  and  $\eta + d\eta$  in the unconstrained system is

$$p(\eta) d\eta = \exp[-\beta F_L(\eta)] d\eta / Z \quad (20)$$

with

$$Z = \int \exp[-\beta F_L(\eta)] d\eta. \quad (21)$$

Now let us consider the quantity

$$h = - \int p(\eta) \ln p(\eta) d\eta. \quad (22)$$

$h$  is obviously a property of the system (molecule plus bath) rather a property of our knowledge about it. In the words of Denbigh and Denbigh[14] it is an objective property rather than a subjective property. As  $p(\eta)$  is a density rather than a dimensionless property,  $Z$  has the dimensions of the order parameter and so the zero of  $h$  depends on the units of  $\eta$ .

Using the expressions above

$$h = \beta \left[ \int p(\eta) F_L(\eta) d\eta - F_{\text{conf}} \right] \quad (23)$$

or

$$h = \beta [\langle F_L(\eta) \rangle - F_{\text{conf}}], \quad (24)$$

the difference of the average Landau free energy and the configurational free energy of the unconstrained system. However as  $F = U - TS$  and the average energy is the same whether calculated by averaging over the constrained systems or over the unconstrained system,  $h$  is the difference of the entropy of a constrained system averaged over all constrained systems and the total entropy,

$$h = [\langle S_L(\eta) \rangle - S_{\text{conf}}]/k_B. \quad (25)$$

Here  $S_L$  is the entropy of a constrained system with fixed  $\eta$ , and the angular brackets denote an average over all constrained systems weighted with their probabilities in the unconstrained system. Thus  $h$  can be interpreted as the entropy associated with the order parameter distribution.

The Shannon information entropy is defined in terms of the information that one has about the system. For example if a histogram of probabilities of  $\eta$  is constructed with bin widths  $\delta$  and if one calculates the Shannon entropy using natural logarithms rather than logarithms to base 2,

$$h_S = - \sum p_i \ln p_i, \quad (26)$$

then

$$\begin{aligned} h_S &\approx \int p \ln p d\eta - \ln(\delta) \\ &= h - \ln(\delta). \end{aligned} \quad (27)$$

Thus the Shannon entropy,  $h_S$ , which is a property of the information collected about the system, provides an approximation to the system property  $h$ . The latter is a measure of the spread of the order parameter. This treatment may readily be extended to more than one order parameter.

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Table 1: Intermolecular Lennard-Jones site-site parameters for water. Cross terms in the Lennard-Jones interactions were calculated using the Lorentz-Bertholet rules.

atoms $i$	$\epsilon_{ii}/\text{kJ mol}^{-1}$	$\sigma_{ii}/\text{\AA}$	$q(i)/e$
O	0.6502	3.169	$-0.8476\lambda$
H	0	0	$0.4238\lambda$
I	0.4184	5.167	varies

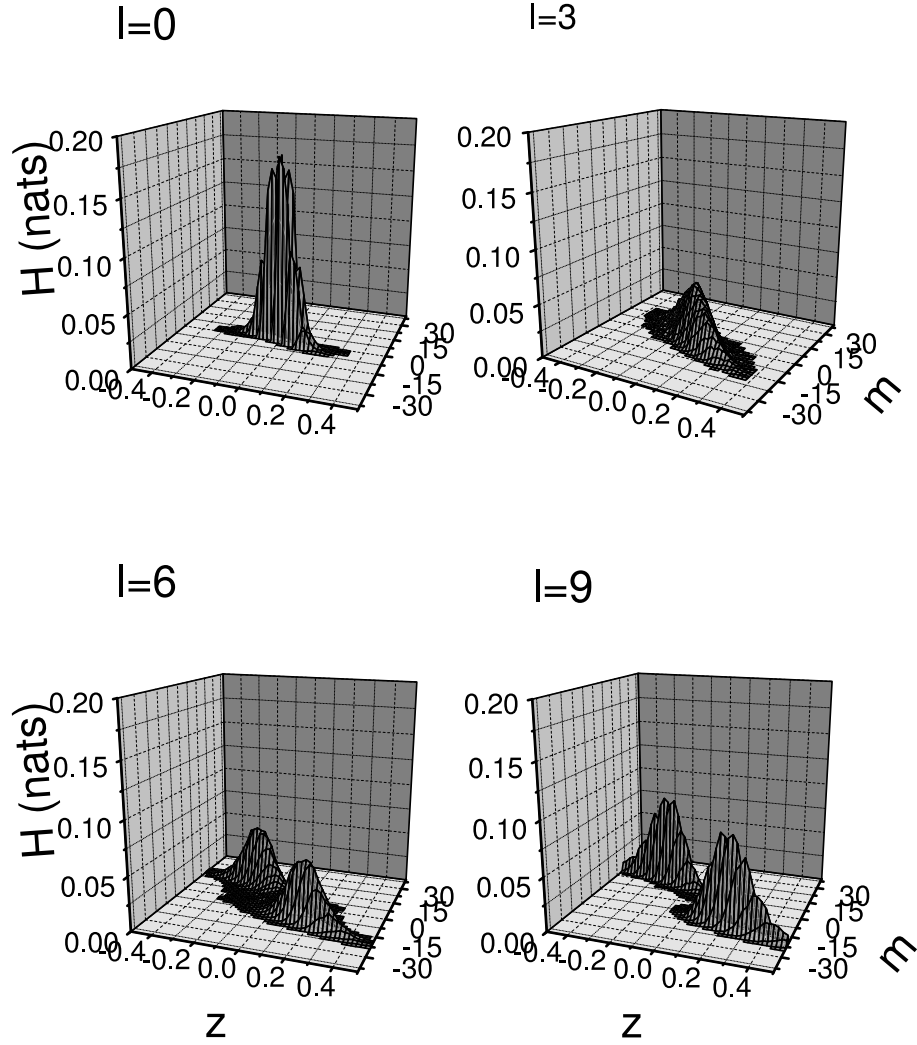


Figure 1: Three-dimensional plots of Shannon's information entropy function  $H(\zeta, \mu)$  of  $I_3^-$  at 300 K as a function of the antisymmetric vibrational normal coordinate  $\zeta$  and the dipole moment  $\mu$  for different modified water solvents. The distributions correspond to charge scaling factors  $\lambda = 0, 0.375, 0.75, 1.125$  (from top to bottom, and left to right). Note the gradual changes from a single peak (symmetry preserving) to double peaks (symmetry breaking) and also the changes of distortions around each peak.

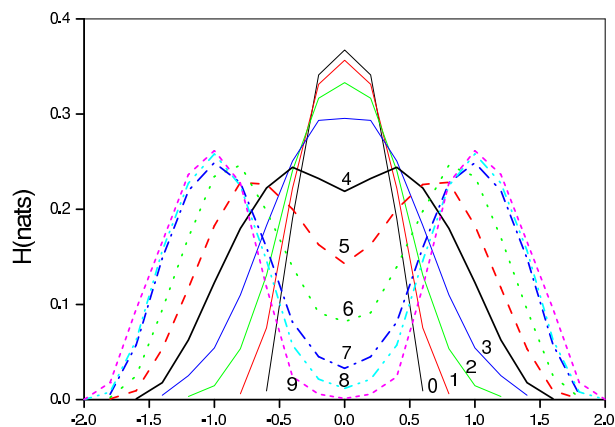


Figure 2: Cross sections through the Shannon entropy function surfaces for different  $\lambda$  values. The curves are labelled with  $\ell = 8\lambda$ . Note that symmetry breaking first occurs when  $\ell = 4$  ( $\lambda = 0.5$ ).

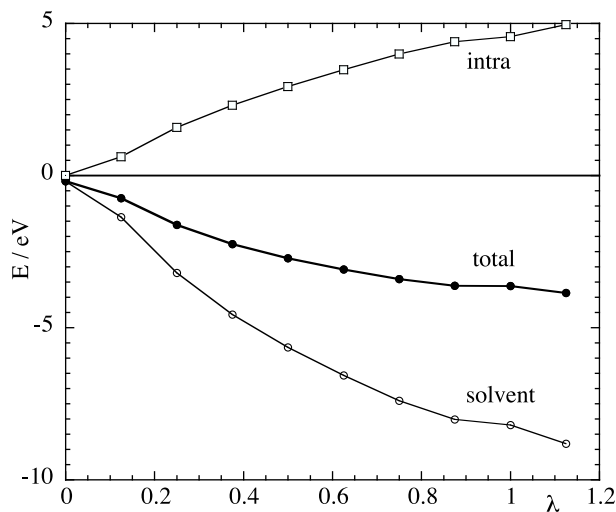


Figure 3: Solvent-solute energetics. The upper curve (triangles) shows the change in the average internal energy of the molecule relative to the gas phase which is a measure of the cost of polarising the molecule. The lowest curve (squares) shows the average solute-solvent interaction energy and the middle curve (circles) shows the sum of these two energies, as a function of  $\lambda$ .

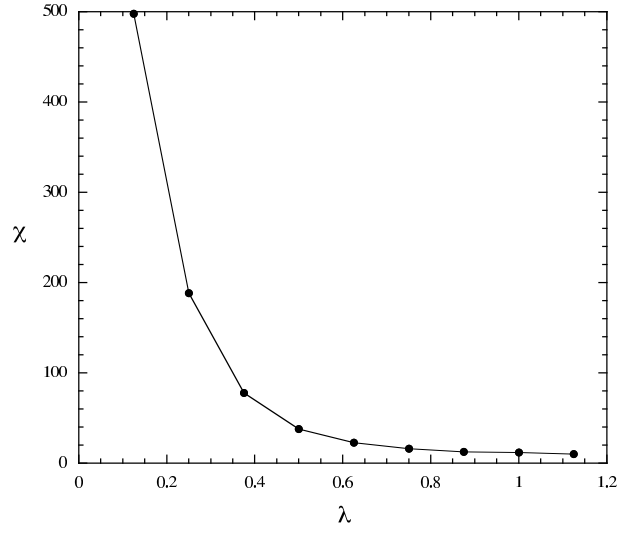


Figure 4: Inverse susceptibility of the triiodide ion in solution as a function of  $\lambda$ .

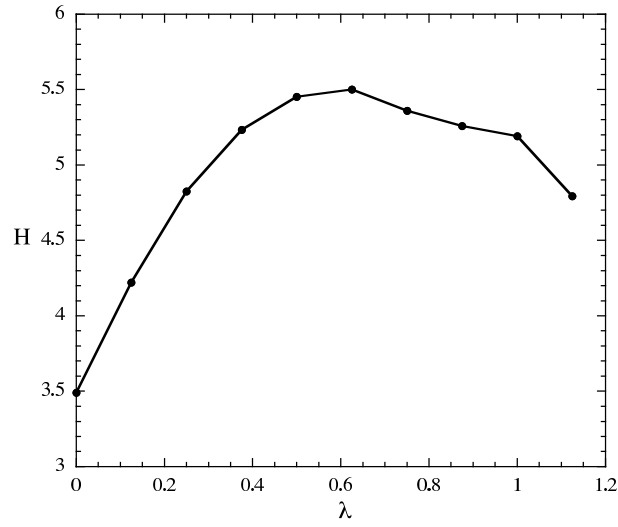


Figure 5: Total Shannon entropy  $h$  as a function of  $\lambda$  for a triiodide ion in solution. Note that there is a weak maximum at about  $\lambda = 0.6$  although the critical value of  $\lambda$  for symmetry breaking lies between  $\lambda = 0.375$  and  $0.5$ .

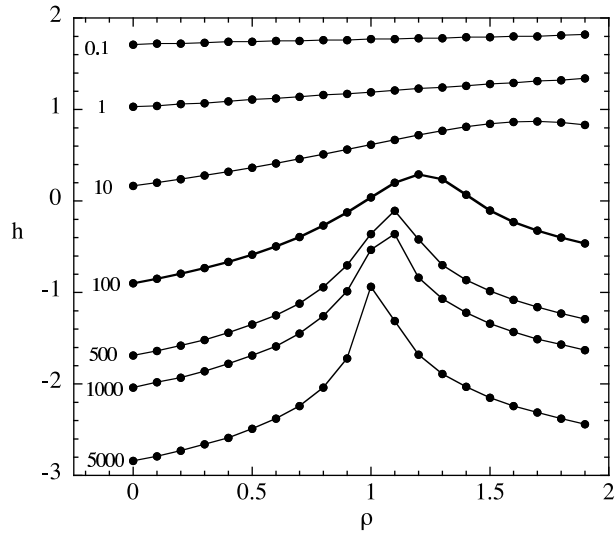


Figure 6: Variation of the entropy associated with the order parameter,  $h$ , with relative solvent strength  $\rho$  for different values of the parameter  $\beta$ . Note that as  $\beta$  increases the maximum gets sharper and moves closer to the critical value  $\rho = 1$ .

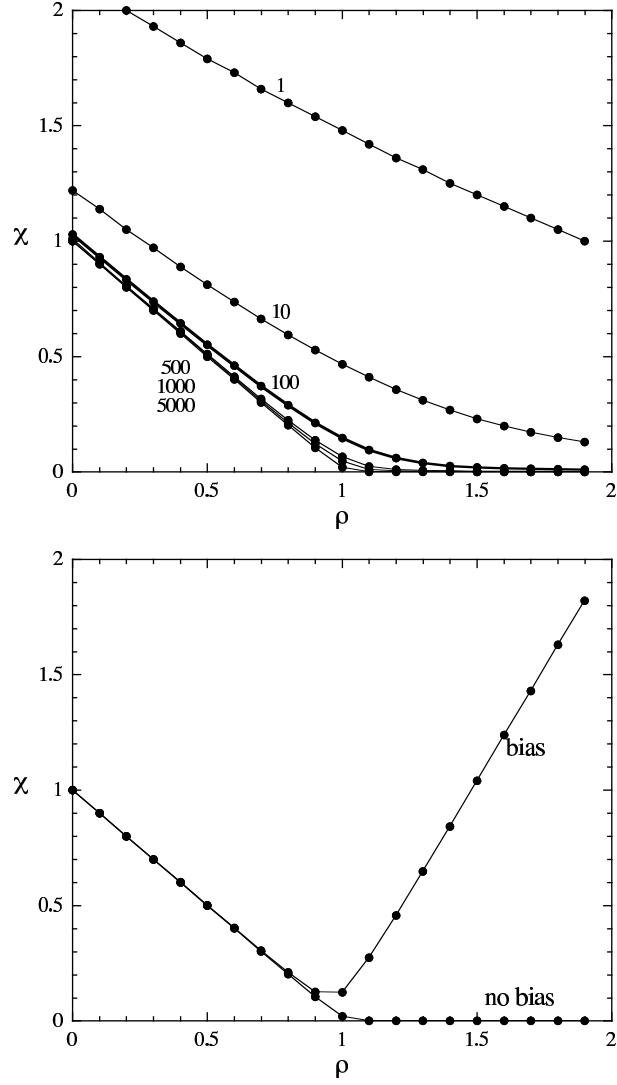


Figure 7: Inverse susceptibility of the model as a function of the solvent strength. Above: results for various values of the parameter  $\beta$ . Below: Results for a high value of  $\beta$  with and without a small biasing field. Note that with the biasing field the model has a minimum inverse susceptibility near the critical value  $\rho = 1$ . In the absence of the biasing field there is a linear decrease in the inverse susceptibility between  $\rho = 0$  and  $\rho = 1$ .